REMARKS

Claims 1-48 are in the case and have been amended to avoid multiple dependent claims. Please calculate the fee based on no multiple dependent claims, and if any multiple dependent claims remain, it is requested that they be amended to depend from lowest numbered claim referred to.

Respectfully submitted,

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Method for producing coated substrates

Field and Background of the Invention

The present invention relates to a method for producing material-charged substrates in which

a) at least one substrate is introduced into an evacuated vacuum container;

b) the surface of the substrate to be charged is exposed to a reactive gas which is adsorbed on the surface;

c) the exposure of the surface to the reactive gas is terminated,

d) the reactive gas adsorbed on the surface is allowed to react.

Such a method is prior known from US 5 916 365. Therein a substrate is introduced into an evacuated vacuum container with a container wall comprised of ceramics, delimiting the process volume against the environment.

The surface to be coated of the substrate is exposed to a first reactive gas, which is adsorbed on said surface. The exposure of the surface to the reactive gas is terminated by subsequently pumping off the reactive gas.

A second reactive gas is subsequently introduced and, by means of a coil configuration provided outside of the vacuum container, an electromagnetic high-frequency field is generated in the container. Thereby at least a portion of the introduced second reactive gas is activated to form radicals, and the first reactive gas adsorbed on the surface, is allowed to react exclusively with said radicals generated by the effect of the high-frequency field.

The present invention addresses the problem of proposing a method of the above listed type, which builds on the deposition of a monolayer of atoms on the surface of the substrate to be coated, but has a substantially expanded flexibility of application with respect to the variety of monolayers which can be deposited.

Summary of the Invention

We are herein addressing charging with materials for the reason that said monolayer does not need to be deposited as a continuous layer in the sense of a coating, but rather the density of deposited atoms can be far lower than is necessary for the formation of a continuous layer. But, if desired, the material charging can readily take place such that a continuous monolayer is formed, in this case in the sense of a coating.

This is attained according to the invention thereby that

d_1) the surface with the adsorbed reactive gas is exposed to a low-energy plasma discharge with ion energy E_{I0} on the surface of the substrate of

$$0 < E_{I0} \leq 20 \text{ eV}$$

and an electron energy E_{eo} of

$$0 \text{ eV} < E_{eo} \leq 100 \text{ eV},$$

d_2) the adsorbed reactive gas is allowed to react at least with the cooperation of plasma-generated ions and electrons.

In contrast to said US 5 916 365 where the adsorbed gas is exclusively allowed to react with radicals, which by definition are electrically neutral, according to the invention the reactive gas adsorbed on the surface is also allowed to react mildly through the effect of ions and electrons generated by low-energy plasma discharge. Therewith the feasibility is given of properly stabilizing the adsorbed gas also without effect of radicals of a further reactive gas on the surface, solely through "mild" interaction with low-energy inert gas ions and electrons or through such effect by other reactive gas ions.

Although the cited US 5 916 365 explains that it was prior known to deposit thin coatings with the inclusion of a glow discharge in an atmosphere of a mixture of reactive gases, but which did not lead to satisfactory coating formation, in the course of the present description it will be explained how the plasma discharge employed

dynamically. In a further preferred embodiment the cathode-anode gap for the plasma discharge is disposed essentially perpendicularly and preferably centrally with respect to said surface.

In a further preferred embodiment of the method according to the invention, during the generation of the plasma discharge a magnetic field is generated in the process volume and the plasma density distribution along the surface is adjusted or controlled stationarily and/or dynamically by means of this field. The plasma density distribution is preferably at least locally wobbled, leading to an effect as if the substrate held stationarily in the plasma were moved with respect to the discharge.

Moreover, preferably at least the reactive gas or gas mixture to be adsorbed is introduced into the process volume such that it is distributed, preferably with an inflow direction substantially parallel to the substrate surface and, further preferred, with injection sites equidistant from the substrate surface. In an especially preferred embodiment of said method, the substrate is formed by a silicon oxide-coated substrate with channels sunk into the silicon layers, wherein after carrying out n-times the step d_2) copper is deposited into the channels. In every case n is therein greater than 1.

Brief Description of the Drawings

In the following the invention will be explained in conjunction with Figures. Therein depict:

Fig. 1 schematically a first embodiment variant of a process module for carrying out the method according to the invention, in particular its phases Ph_1 and/or Ph_2,

Fig. 2 in a representation analogous to that of Figure 1, a preferred embodiment variant of the process module according to Figure 1,

Fig. 3 in a representation analogous to Figure 1 or 2, a further type of process module for carrying out cleaning steps by the method according to the invention,

Fig. 4 in a representation analogous to Figures 1 to 3, a modification of the process module depicted in Figure 3,

Fig. 5 simplified a preferred embodiment of a process module according to Figure 2, convertible into a process module according to Figure 3 or 4,

Fig. 6 with respect to a nozzle axis A of the process module according to Figure 5, the spatial and time modulation caused by the control of components of the magnetic field parallel to axis A over a plane E, perpendicularly to nozzle axis A,

Fig. 7 by example and schematically a method according to the invention for multilayer realization,

Fig. 8 a further embodiment of a method according to the invention with multilayer realization, and

Fig. 9 in top view and simplified the combination of process modules according to Figures 1 to 5 to form a circular or cluster installation for carrying out the method according to the invention.

Description of the Preferred Embodiments

In Figure 1 is schematically depicted a process module of type I preferably employed for carrying out the method according to the invention. A chamber wall 1 of a vacuum container 3 encompasses a process volume PR. In the process volume PR is provided a substrate carrier 5. The process volume PR is pumped down via a pumping connection 11, such as is shown schematically with vacuum pump 13, to

Patent Claims

1. Method for producing substrates charged with materials, in which
   a) at least one substrate is introduced into an evacuated vacuum container;
   b) the surface of the substrate to be charged is exposed to a reactive gas which is adsorbed on the surface;
   c) the exposure of the surface to the reactive gas is terminated,
   d) the reactive gas adsorbed on the surface is allowed to react,
   characterized in that
   d_1) the surface with the adsorbed reactive gas is exposed to a low-energy plasma discharge with ion energy E_{I0} on the surface of the substrate of
   $$0 < E_{I0} \leq 20 \text{ eV}$$
   and an electron energy E_{eo} of
   $$0 \text{ eV} < E_{eo} \leq 100 \text{ eV};$$
   d_2) the adsorbed reactive gas is allowed to react at least with the cooperation of plasma-generated ions and electrons.

2. Method as claimed in claim 1, characterized in that the plasma discharge is realized with an ion energy E_{Io} on the surface of the substrate of
   $$0 \text{ eV} < E_{Io} \leq 15 \text{ eV}.$$

3. Method as claimed in [one of claims 1 or 2] claim 1, characterized in that the adsorbed reactive gas is a reactive gas mixture.

4. Method as claimed in [one of claims 1 to 3] claim 1, characterized in that the plasma discharge is maintained in an inert gas atmosphere.

5. Method as claimed in claim 4, characterized in that the plasma discharge is maintained in an argon atmosphere.

6. Method as claimed in [one of claims 1 to 5], characterized in that the plasma discharge is generated in an atmosphere which contains a further reactive gas or gas mixture.

7. Method as claimed in claim 6, characterized in that the further reactive gas or gas mixture contains at least one of the gases hydrogen, nitrogen, oxygen.

8. Method as claimed in claim 6, characterized in that the further reactive gas or gas mixture comprises hydrogen, preferably is hydrogen.

9. Method as claimed in [one of claims 1 to 8], characterized in that the vacuum container is evacuated to a pressure (p_v) for which applies:

$$10^{-11} \text{ mbar} \leq p_v \leq 10^{-8} \text{ mbar}.$$

10. Method as claimed in [one of claims 1 to 9], characterized in that the reactive gas to be adsorbed is allowed to flow in up to a partial pressure p_p, for which applies:

$$10^{-4} \text{ mbar} \leq p_p \leq 1 \text{ mbar}.$$

11. Method as claimed in [one of claims 1 to 10], characterized in that the gas adsorption rate on the surface is controlled by heating/cooling the surface.

12. Method as claimed in [one of claims 1 to 11], characterized in that the exposure is terminated thereby that the substrate is transferred from the evacuated vacuum container into a further evacuated vacuum container.

13. Method as claimed in [claim 1 one of claims 1 to 12], characterized in that the exposure of the surface is terminated by pumping out the remaining adsorbed reactive gases from the evacuated vacuum container.

14. Method as claimed in claim 13, characterized in that the reactive gas is pumped out until a pressure p_v' is reached for which applies:

$$10^{-11} \text{ mbar} \leq p_v' \leq 10^{-8} \text{ mbar}.$$

15. Method as claimed in claim 1 [to 14] characterized in that the substrate is exposed to the plasma treatment at least during a predetermined minimum time period.

16. Method as claimed in [claim 1 one of claims 1 to 15], characterized in that at least the steps b) to d_2) are completed at least twice.

17. Method as claimed in [claim 1 one of claims 1 to 16], characterized in that after carrying out at least one step d_2), a different material is applied onto the surface.

18. Method as claimed in claim 17, characterized in that the further material is applied by means of a vacuum coating process, by means of wet chemistry or galvanically.

19. Method as claimed in [claim 1 one of claims 1 - 18], characterized in that before the exposure of the surface to the reactive gas to be adsorbed, the surface is exposed to a low-energy inert gas plasma, preferably an argon plasma, with ion energies E_{I1} on the surface of

$$0 \text{ eV} < E_{I1} \leq 20 \text{ eV}$$

preferably

$$0 \text{ eV} < E_{I1} \leq 15 \text{ eV}$$

and an electron energy E_{e1} of

$$0 \text{ eV} < E_{e1} \leq 100 \text{ eV}.$$

20. Method as claimed in [one of claims 1 - 19], characterized in that before the exposure of the surface to the reactive gas to be adsorbed, the surface is exposed to a low-energy plasma discharge in an atmosphere comprising a further reactive gas, where for the ion energy E_{I2} applies:

$$0 \text{ eV} < E_{I2} \leq 20 \text{ eV},$$

preferably

$$0 \text{ eV} < E_{I2} \leq 15 \text{ eV}$$

at an electron energy E_{e2} of

$$0 \text{ eV} < E_{e2} \leq 100 \text{ eV}.$$

21. Method as claimed in claim 20, characterized in that the further reactive gas is at least one of the gases hydrogen, nitrogen, oxygen.

22. Method as claimed in claim 20, characterized in that the further reactive gas comprises hydrogen, preferably is hydrogen.

23. Method as claimed in [one of claims 1 - 22], characterized in that after the reaction of the adsorbed reactive gas, the surface is exposed to a low-energy inert gas plasma, preferably argon plasma, with an ion energy E_{I3} on the surface of

$$0 \text{ eV} < E_{I3} \leq 20 \text{ eV},$$

preferably

$$0 \text{ eV} < E_{I3} \leq 15 \text{ eV}$$

and an electron energy E_{e3} of

$$0 \text{ eV} < E_{e3} \leq 100 \text{ eV}.$$

24. Method as claimed in [claim 1 one of claims 1 - 23] characterized in that after the reaction of the adsorbed reactive gas, the surface is exposed to a low-energy plasma discharge in an atmosphere which comprises a further reactive gas, wherein for the ion energy E_{I4} on the substrate surface applies:

$$0 \text{ eV} < E_{I4} \leq 20 \text{ eV},$$

preferably

$$0 \text{ eV} < E_{I4} \leq 15 \text{ eV}$$

and with an electron energy E_{e4} of

$$0 \text{ eV} < E_{e4} \leq 100 \text{ eV}.$$

25. Method as claimed in claim 24, characterized in that the further reactive gas is at least one of the gases hydrogen, nitrogen, oxygen.

26. Method as claimed in claim 24, characterized in that the further reactive gas comprises hydrogen, preferably is hydrogen.

27. Method as claimed in [claim 1 one of claims 1 - 26], characterized in that the surface charging takes place by means of at least one of the following materials:

oxides or nitrides or oxinitrides of Si, Ge, Ti, Ta, Hf, Zr, Al, Nb, W and/or of the following metals:
Al, Ti, Cu, W, Ta.

28. Method as claimed in claim 27, characterized in that the surface charging takes place by means of at least one of the following materials:

silicon oxide, tantalum oxide, zirconium oxide, titanium nitride, tantalum nitride, tungsten nitride, $(TaSi)_xN_y$.

29. Method as claimed in [one of claims 1 - 26], characterized in that all method steps are carried out in one vacuum container.

30. Method as claimed in [one of claims 1 - 26], characterized in that the method steps are carried out in at least two vacuum containers.

31. Method as claimed in [one of claims 1 to 30], characterized in that the process atmosphere encompassing the surface of the substrate during at least one of the phases comprised of steps b) and c) and/or d) to d_2), is isolated from the inner wall of a vacuum container at ambient surroundings.

32. Method as claimed in [one of claims 1 to 31], characterized in that the surface to be charged includes the surface of a substrate already charged or coated.

33. Method as claimed in [one of claims 1 to 32] characterized in that the surface before the adsorption step and/or after the reaction of the adsorbed reactive gases or gas mixture is exposed to a plasma-enhanced cleaning step, in which in a reactive gas or gas mixture - preferably comprising hydrogen - it is activated by means of a low-energy plasma discharge with ion energy E_r on the substrate surface of

$$0 \text{ eV} < E_r \leq 20 \text{ eV},$$

preferably

$$0 \text{ eV} < E_r \leq 15 \text{ eV}$$

at an electron energy E_{er} of

$$0 \text{ eV} < E_{er} \leq 100 \text{ eV}.$$

34. Method as claimed in claim 33, characterized in that during the at least one cleaning step the cleaning process atmosphere is isolated by means of a metallic encapsulation from the inside wall of the cleaning vacuum container

at ambient surrounding or this process atmosphere is directly preferably delimited by the inside wall of a cleaning vacuum container at ambient surroundings.

35. Method as claimed in [one of claims 1 to 34] claim 1, characterized in that through a single sequence of steps a) to d_2) one atom monolayer is applied onto the surface.

36. Method as claimed in [one of claims 1 to 35] claim 1, characterized in that by repeating steps b) to d) an epitaxial layer is grown on, with a change of the reactive gas heteroepitaxial ones, without a change of the reactive gas homoepitaxial ones.

37. Method as claimed in [one of claims 1 to 36] claim 1 characterized in that after carrying out a predetermined number of passes through steps b) to d) sequentially on several substrates the process volume of the vacuum container is subjected to a plasma-enhanced process volume cleaning step without an introduced substrate or with a substrate dummy, which process volume cleaning step preferably first comprises an etching step, subsequently a cleaning step, preferably in a plasma comprising hydrogen, inert gas or a mixture thereof.

38. Method as claimed in [one of claims 1 to 37] claim 1, characterized in that before step a) and/or after step d_2) the substrate is subjected to a substrate cleaning step after being spatially separated from the vacuum container and that the transport of the substrate there between is carried out under vacuum.

39. Method as claimed in claim 38, characterized in that the transport under vacuum takes place at least piecewise linearly or preferably along a circular path, with linear guide movements to said containers, preferably with motion components radial with respect to a circular path.

40. Method as claimed in claim 1 one of claims 1 to 39, characterized in that during steps b) to and including d) the process atmosphere to which is exposed the surface is isolated from the inner wall of a vacuum container at ambient surrounding by means of a surface which in the new condition is chemically inert against the reactive gas or gas mixture and/or against a second plasma-activated reactive gas or gas mixture, preferably by means of a dielectric or graphitic surface.

41. Method as claimed in claim 40, characterized in that the inert surface is the surface of a partition wall which is spaced apart from the inner wall of the vacuum container along predominant surface sections.

42. Method as claimed in at least claim 40 one of claims 40 or 41, characterized in that the surface for isolation in the new condition is realized of at least one of the following materials:
quartz, graphite, silicon carbide, silicon nitride, aluminum oxide, titanium oxide, tantalum oxide, niobium oxide, zirconium oxide or a layered combination of these materials, in this case also with diamond-like carbon or diamond.

43. Method as claimed in claim 1 one of claims 1 to 42, characterized in that the plasma discharge is realized with an electron source with electron energy $E_e \leq 50$ eV, in particular preferred by means of a DC discharge.

44. Method as claimed in Claim 1 one of claims 1 to 43, characterized in that the plasma discharge is realized by means of a thermionic cathode, preferably with a directly heated thermionic cathode.

45. Method as claimed in [claim 1 one of claims 1 to 44], characterized in that in the process volume of the vacuum container for the plasma discharge at least two anodes spatially offset and preferably each heatable are provided, preferably each electrically actuatable separately and through the control of the electric potentials impressed thereon and/or their temperature the plasma density distribution along the surface is dynamically adjusted or controlled along the surface.

46. Method as claimed in [claim 1 one of claims 1 to 45], characterized in that during step d) in the process volume a magnetic field is generated and by means of this magnetic field the plasma density distribution along the surface is stationarily and/or dynamically adjusted or controlled, preferably at least such that it wobbles locally.

47. Method as claimed in [claim 1 one of claims 1 to 46], characterized in that at least the reactive gas or gas mixture to be adsorbed is allowed to flow distributively into the process atmosphere, preferably with a direction of inflow substantially parallel to the surface and, further preferred, with injection sites equidistant from the surface.

48. Method as claimed in [claim 1 one of claims 1 to 47], characterized in that the substrate is a silicon oxide-coated substrate with grooves sunk into the silicon oxide layer, and that after carrying out n-times one of the steps d_2), copper is deposited in the grooves, where $n \geq 1$.

cancel 49. Use of the method as claimed in one of claims 1 - 48 for the production of relaxed buffers.